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(54) Title: VOLATILE GLASS BATCH MATERIALS INCORPORATED IN FRITS

(57) Abstract

This invention is directed to a process of adding amorphous glass frits which contain a large concentration of normally volatile materials, e.g., colourants like selenium, into the glass forming components present in a glass melting furnace during glass formation. Including the normally volatile materials in this frit form significantly lowers the volatility of those materials, which otherwise normally revert to the gaseoius state at the high operating furnace temperatures. Examples of some generally used batch materials that normally volatilise from the glass batch and hence are particularly suitable for incorporation in the amorphous glass frit, include selenium, lead oxide, zinc oxide, boron oxide, sulphates, fluorides, chlorides, bromides, iodides, phosphates and mixtures thereof.

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VOLATILE GLASS BATCH MATERIALS INCORPORATED IN FRITS

This invention relates to the use of amorphous glass frits containing an increased concentration of normally volatile glass batch material, e.g., selenium or boron oxide, as a source of the volatile material in molten glass preparation.

In order to make glass compositions, for example, soda-lime-silica glass compositions, batch materials like sand, soda ash, limestone, dolomite and colourants, like selenium, are combined and subjected to extremely high temperatures to melt the materials. During this high temperature melting process, a portion of some of the solid materials volatilise when being converted to the glassy liquid state. Such volatilised materials exit out through the furnace exhaust system with other gases and hence are essentially lost from the glass melt. This volatilisation and hence removal of materials which are a vital part of the final glass product requires that excess quantities of the batch material must be included in the batch to ensure that the final product has the desired amount of the material. This leads to an increased cost to manufacture the product and an extra expense and effort in collecting volatile components if regulations prevent their disposal in the atmosphere. In addition, many volatile materials have a corrosive action to certain refractories used in the glass making process. Therefore, it is very desirable to improve the retention of volatile constituents in the glass product.

One normally highly volatile component employed in some glass compositions is selenium. When selenium is added to the batch as elemental selenium, about 80-90% is converted to the gaseous state and hence essentially 80-90% of the added selenium is vaporised out of the batch. The problem is exacerbated when the glass tank is heated by overhead gas flames which sweep across the surface and help

to physically remove such vaporised materials whilst batch materials are being converted into the glassy state.

The present invention overcomes the problems discussed above by using, as the source of normally volatile glass batch material, an amorphous glass frit containing an increased concentration, i.e., a concentration above that desired in the final glass composition, of such normally volatile glass batch material. When this frit, containing normally volatile batch material, is added to the batch during glass making, more of the normally volatile material is retained in the molten glass batch. The present inventors believe that having the normally volatile batch materials in an amorphous (glassy) state makes it much more difficult for any volatile components to leave the glass batch composition during melt processing thereof.

Glass frits of agglomerated sintered materials, not amorphous glass frits as in the present invention, have previously been used in the glass industry added to the molten glass in the forehearth, i.e., at a point in the process where the molten glass has exited the batching furnace and is being cooled. Such agglomerated glass frits are in contrast to the present invention frits which are amorphous glass frits, i.e., the normally volatile species must be in the glassy state. U.S. Patent 2,955,948 to Silverman describes forming an agglomerated frit consisting essentially of selenium, niter, and arsenic oxide. Such frits are added to the forehearth rather than the glass batch furnace, i.e., to a molten base glass composition exiting the batching furnace. This process allows forming glass of various colours without converting the complete glass batch in the furnace to one particular colour.

In U.S. Patent 3,291,585, Okamura discloses a sintered frit made by mixing pulverised glass cullet together with the additive ingredient, i. e. selenium, and sintering at 500°C to 1200°C. Okamura in '585 states: " According to the sintering, a part of the additive ingredient is dissolved into the glass cullet, another part

is absorbed and a further part is occluded in the interior thereof in a gaseous state..." Glass frit used in our invention, in contrast, is present in totality as an amorphous glass frit. U.S. Patent 3,628,932 to Inoue describes another method of making a sintered frit which comprises separating a portion of the raw batch, adding selenium and a source of alkali metal oxide in an increased percentage over that desired in the final molten product, and sintering at 500°C to 1000°C. Inoue teaches that the sintered product containing the increased alkali metal oxide, when used as the selenium source, provides doubled selenium retention when compared to using metallic selenium as the raw material source. We have found that using present invention amorphous glass frits containing selenium provides selenium retention improved even over that of the Inoue invention sintered product.

The present invention is directed to a process which comprises adding an amorphous glass frit containing normally volatile glass batch materials into the glass forming components present in a melting furnace during molten glass formation, the normally volatile batch material being present in the amorphous glass frit in a percentage by weight at least two times as large as that desired in the final molten glass product. Herein, "amorphous glass frit" means a frit of a base glass composition (e.g., a soda-lime-silica glass) including an increased concentration of a normally volatile glass batch material (e.g., selenium), in amounts as defined above. Still another aspect of this invention comprises the glass product melt made by incorporating the amorphous glass frit into the glass components in the melting furnace during the glass making process.

As disclosed above, the present invention is directed to a process which comprises adding an amorphous glass frit containing normally volatile glass batch material into a glass melting furnace during molten ~~glass~~ formation as

disclosed above. This frit is completely amorphous (glassy) and not merely sintered into an agglomerated frit as is the case with many prior art frits. The frit used in the present invention, when added to the other raw batch materials (glass components) in the glass melting furnace, goes through the same melting schedule and temperature sequences as the batch components. We have unexpectedly discovered that once a normally volatile material (i.e., normally volatile at the processing temperatures of the glass melting furnace) becomes an integral part of a glass (i.e., the amorphous glass frit), it is exceedingly much more difficult for that volatile material to leave the glass melt during subsequent melting. It appears that the normally volatile material has become chemically integrated, to some extent, into the glass matrix. Thus, a much greater proportion of the volatile material will be retained in the molten product.

Selenium can be used as a model of the unexpected improvement shown according to the present invention. This is because in conventional batch processing selenium addition is by means of metallic selenium added into the melting furnace as a raw material and only from 10 to 20% of the selenium from the batch is retained in the final molten glass product. That means that in conventional glass processing, the batch must include 5 to 10 times the amount of raw material selenium than is necessary in the final molten glass product. The excess amount of selenium simply goes into the atmosphere and is exhausted out of the stack. Using an embodiment of the present invention, amorphous selenium frit, eliminates a large proportion of the normal selenium emissions associated with using elemental selenium. Selenium is sometimes present in a compound which, when added as a batch material, also loses a large proportion of the volatile selenium in the process of becoming part of the glass composition. As shown in Examples 1-20 herein, we have found that glass melts made with amorphous selenium frits according to our invention show selenium retention

which is improved by a factor of 2 to 11 compared to glass melts made conventionally using only elemental selenium.

The present invention process uses amorphous glass frit which comprises a concentration of the normally volatile material in the amorphous state incorporated in a glass composition generally of the type of the intended glass product. For example, if the invention amorphous glass frit containing selenium was being employed in colouring a soda-lime-silica glass, the frit would generally include an increased concentration of the colourant, selenium, in a soda-lime-silica glass. As disclosed above, the normally volatile batch material is present in the amorphous glass frit in a percentage by weight at least two times as large as that desired in the final molten glass product. Preferably, the percentage of volatile material in the frit is at least ten times as large as that desired in the final molten melt. As would be appreciated by those skilled in the art in view of the present disclosure, the optimal amount of each of the materials incorporated in the amorphous glass frit is independently selected and will depend on various factors including meltability of the frit. While selenium has been used as a model of a volatile material whose incorporation into an amorphous glass frit will improve retention of that material when the frit is used to add that material to the glass batch, the volatile materials that can be used in the frit are not so limited. For example, the frit used in this invention may include, but is not limited to, materials like lead oxide, zinc oxide, boron oxide, sulphates, fluorides, chlorides, bromides, iodides, phosphates, and suitable mixtures thereof.

Exemplary of a particularly useful selenium embodiment of the invention frit comprises a relatively high concentration of selenium, at least about 1.0 percent by weight, based on the total weight of the amorphous glass frit. Selenium is such a strong colourant that it has been used in glass compositions at concentrations as low as

0.0002 to 0.0035 weight % to impart a strong absorption in the spectral transmission between 400 and 500 nanometres.

Many of the glass compositions that include selenium as a colourant also include iron oxide as a colourant. We have also discovered that the retention of selenium is further improved when the equilibrium of iron oxide, if also present in the molten glass, is shifted toward the oxidised state. Some methods used to shift the iron oxide equilibrium during melting include adding to the melt an oxidiser such as sodium or potassium nitrates or to maintain oxidising conditions in the furnace firing. We have found that there is a linear improvement in selenium retention as the iron equilibrium is shifted toward the oxidising portion of iron. The amorphous glass frit containing selenium can still be used in glass compositions not employing iron oxide as a colourant.

In forming an amorphous glass frit useful in the present invention process, generally the glass batch materials including the normally volatile material is first heated and melted into an amorphous glass melt and subsequently the melt is rapidly quenched to form the frit. This cooling may be done, e.g., by subjecting the melt to cold water. As mentioned above, the normally volatile component, e.g., selenium, is included into the amorphous glass frit at a much higher concentration that will be found in the final product glass made with the invention frit.

Exemplary of one preferred method of forming the amorphous glass frit employs a cold-top melter and is described as follows: premixed glass batch components are fed on the top of a molten glass mass that is heated below the glass level via electrodes. The batch layer completely covers the molten glass providing an insulating barrier and the top of the batch is relatively cool which generates the name "cold-top melter". The cold-top melter is extremely effective in retaining a volatile species in that the thick layers of batch form a pseudo chemical retort where volatile gases vaporise near the hot glass melt surface only to

condense as the vapours meander up through the insulating batch cover and condense back to the solid state. When the top of the batch layer is below the boiling point of the volatile component; nearly 100% of the gaseous material will condense in the batch layer. This amorphous melt would subsequently be converted to frit by quenching as disclosed herein. While the above process for forming the amorphous glass frit is particularly desirable, the process for forming the frit used is not critical to this invention. As would be apparent to those skilled in the art in view of this disclosure, there are a variety of methods that can be used to generate the frit used in the process of this invention.

The critical factor in our invention is that we have unexpectedly discovered that glasses made with amorphous glass frits as the source of normally volatile batch materials retain a much greater proportion of the volatile material in the final molten glass product than when the volatile material is used as a raw batch material (i.e., not incorporated in an amorphous glass frit). The very nature of volatile components introduced into a glass product is that a portion of the volatile component is lost to the atmosphere in the process of converting batch materials via high temperature furnace to a glass product. As would be appreciated, when the normally volatile materials remain in the glass, there are lower emissions of the volatile materials which may eliminate the necessity to collect the emissions. Additionally, since some volatile glass material species also chemically attack the refractory materials meant to contain them, the ability to employ lower concentrations of such volatile materials as part of the batch components will lead to an extended useful life of the furnace since the rate of corrosion will be reduced.

The following procedure is used in making the examples of TABLES III-VII which disclose glass compositions, the odd numbered examples being made according the present invention process and the even numbered examples

being comparative examples. First, the glass ingredients including an amorphous glass frit (which is a base glass composition with selenium) are weighed (typically being 150 grams total) on a laboratory balance and mixed with in a glass jar with a laboratory shaker for 10 minutes each. Each mixed batch is placed into a platinum-rhodium crucible which is about 2" tall with about a 2.5" inside diameter and 4.5 ml. of water is mechanically mixed into the raw batch. The crucibles are placed into a natural gas/air furnace pre-heated to 2600°F with 3 to 5 other crucibles. The furnace temperature recovers to 2600°F in about 30 minutes and the batch materials melt. After two hours of heating the melt, each crucible is removed in turn. The amorphous glass containing the colourant in the crucible is fritted by quenching in cold water to improve the homogeneity of the glass, and the fragments are mixed in the crucible and all crucibles are returned to the furnace. The furnace temperature is brought back to 2600°F, that operating temperature obtained (about 45 minutes), and the melt is heated for one hour. The glass is further melted for 3 hours to form glass composition samples and each sample is poured into a 2.5" inside diameter graphite mould to shape the glass samples for subsequent grinding and polishing. All samples are placed into an annealing furnace, brought up to 1050°F, held for 4 hours, then allowed to slowly cool to room temperature in about 16 hours. The hardened glass samples are ground and polished and spectral properties are measured on each sample; spectral properties are calibrated to a control thickness of 4 mm. The samples may then be chemically analysed via X-ray fluorescence or other tests conducted as needed. The above procedure for making the glass compositions of the examples can also be used, with slight modification, to make the amorphous glass frit used in making the glass. The modification would involve fritting the glass again in cold water and subsequently drying it, after the second fritting and three hours melting discussed above. The amorphous glass frit need not go

through an annealing process as carried out above for the glass compositions and can simply be used in a measured amount as the source of the volatile consitiuent into the glass melt.

All of the glass compositions in Examples 1-20 (as well as embodiments of the present invention amorphous glass frits as shown in Table II) are made based on the following soda-lime-silica glass shown in TABLE I:

TABLE I

Batch Material	Amount in grams
Sand (SiO_2)	100.00
Soda Ash (Na_2CO_3)	31.41
Limestone ($CaCO_3$)	7.25
Dolomite ($Ca*Mg(CO_3)_2$)	25.83

TABLE II

Frit Number	Weight % Selenium
Frit 1	0.42%
Frit 2	0.46%
Frit 3	0.68%
Frit 4	1.12%
Frit 5	2.43%
Frit 6	2.68%

The following examples 1-20 show by way of comparison the improvement which results when glass compositions are made using embodiments of present invention frit to provide selenium colourant (odd numbered examples) as compared to conventional addition of selenium metal (even examples). In Examples 1-20, the base glass is a dark grey glass which uses iron oxide as an additional colourant. In all of

these examples, the batch materials for making the glass are given in the tables below in grams per 100 grams of sand, as done in Table I. The quantities of salt cake (Na_2SO_4), carbocite (anthracite coal containing C), and sodium nitrate ($NaNO_3$), each contribute to controlling the redox ratio of the iron oxide (the redox ratio = FeO/(total iron oxide as Fe_2O_3)) is listed in each of these examples since this redox ratio can effect the selenium retention as disclosed above. In order to be able to draw meaningful conclusions from the comparative glass example pairs, e.g., Example 1 (glass made with selenium frit) and Example 2 (glass made with conventional metallic selenium), the redox ratios as defined above and the total iron oxide as Fe_2O_3 in the final product are nearly identical in each of the comparative pairs. Increasing the salt cake or carbocite lowers the selenium retention while increasing the sodium nitrate improves the selenium retention.

TABLE III

Batch Material	Example 1	Example 2	Example 3	Example 4
Salt Cake	1.0884	1.1045	1.0903	1.1046
Sodium Nitrate	0.5150	0.5251	0.5185	0.5233
Carbocite	0.0644	0.0651	0.0906	0.0923
Se (metal)		0.639		0.1133
Se Frit #1	2.6500		2.3212	
ppm Se Retained in Glass Product	26	28	14	24
% Se Retained in Glass Product	32.03	6.01	19.68	2.90
Total Iron Oxide	1.145	1.160	1.160	1.180
Redox ratio	0.227	0.218	0.260	0.254
Ratio of Retained Se, as Frit/Metal	5.33		6.79	

TABLE IV

Batch Material	Example 5	Example 6	Example 7	Example 8
Salt Cake	1.0922	1.1062	1.0879	1.1050
Sodium Nitrate	0.5180	0.5261	0.5160	0.5245
Carbocite	0.0650	0.0657	0.0645	0.0650
Se (metal)		0.566		0.0639
Se Frit #1	2.6452		2.9900	
ppm Se Retained in Glass Product	23	24	35	31
% Se Retained in Glass Product	28.38	5.80	38.21	6.65
Total Iron Oxide	0.980	0.990	1.052	1.090
Redox ratio	0.227	0.224	0.222	0.217
Ratio of Retained Se, as Frit/Metal	4.89		5.75	

TABLE V

Batch Material	Example 9	Example 10	Example 11	Example 12
Salt Cake	1.0962	1.1036	1.0958	1.1054
Sodium Nitrate	0.5204	0.5244	0.5205	0.5247
Carbocite	0.0913	0.0922	0.0914	0.0651
Se (metal)		0.919		0.0352
Se Frit #2	2.2000		4.4001	
ppm Se Retained in Glass Product	12	33	25	19
% Se Retained in Glass Product	16.26	4.92	16.93	7.30
Total Iron Oxide	1.460	1.440	1.450	1.420
Redox ratio	0.246	0.240	0.238	0.240
Ratio of Retained Se, as Frit/Metal	3.30		2.32	

TABLE VI

Batch Material	Example 13	Example 14	Example 15	Example 16
Salt Cake	1.0966	1.0960	1.0961	1.0966
Sodium Nitrate	0.5191	0.5188	0.5211	0.5203
Carbocite	0.0917	0.0917	0.0910	0.0915
Se (metal)		0.419		0.0841
Se Frit #6	1.2362		1.2360	
ppm Se Retained in Glass Product	26	24	23	22
% Se Retained in Glass Product	42.40	7.85	37.52	3.59
Total Iron Oxide	1.420	1.430	1.430	1.430
Redox ratio	0.226	0.221	0.233	0.242
Ratio of Retained Se, as Frit/Metal	5.40		10.45	

TABLE VII

Batch Material	Example 17	Example 18	Example 19	Example 20
Salt Cake	1.0982	1.1047	1.0961	1.0960
Sodium Nitrate	0.5215	0.5249	0.5193	0.5234
Carbocite	0.0	0.0648	0.0906	0.0913
Se (metal)		0.1057		0.0414
Se Frit #1	2.0691			
Se Frit #6			0.4122	
ppm Se Retained in Glass Product	43	124	8	43
% Se Retained in Glass Product	67.80	16.08	39.13	6.12
Total Iron Oxide	0.579	1.450	1.460	1.460
Redox ratio	0.169	0.165	0.225	0.224
Ratio of Retained Se, as Frit/Metal	4.22		6.39	

In the Examples 1-20, the "Ratio of Retained Se, as Frit/Metal" is obtained by dividing the % Se retained in the comparative pairs. That is, the retained ratio of 5.33 in Example 1 (a Se Frit composition according to the present invention) is obtained by dividing 32.03% by 6.01% and indicates that 5.33 times as much Se is retained in the Example 1 glass as in the comparative Example 2 glass. In reviewing the comparisons of Examples 1-20 of TABLE III through TABLE VII, it has been clearly demonstrated that glass products made with present invention amorphous

selenium frits retain at least twice as much up to about 10.5 times the amount of selenium when compared to conventionally made melts made using elemental selenium as the source of selenium.

These examples further demonstrate that in glass compositions also containing iron oxide, as the iron oxide equilibrium is shifted toward oxidising conditions (i.e., toward smaller redox FeO/Fe_2O_3 ratios), there is a distinct improvement in the retention of selenium in the glass products. The other frits of TABLE II, i.e., Frits 3-5, also showed similar improvements of selenium retention when incorporated in glass melts when compared to glass melts made with conventionally added selenium.

Glass melts made incorporating volatile materials other than selenium are shown in the following tables. The melts in TABLE VIII below were made using embodiments of amorphous glass frits according to the present invention and can be paired for comparison with the melts of TABLE IX made conventionally without the invention frits. That is, Examples 21, 22, and 23 can be paired, respectively, with Examples 24, 25, and 26. The Example 21-23 melts contain 30% frit and 70% batch material. Examples 24-26 melts contain 30% cullet and 70% of batch material. Examples 21 and 24 are based on the same clear boro-soda-lime-silica base glass, Examples 22 and 25 are based on the same clear soda-lime-silica glass, and Examples 23 and 26 are based on the same dark grey soda-lime-silica glass.

TABLE VIII below shows that improvements are achieved in volatile material retention when the glass melts are made using a frit containing a higher concentration of volatile species than that desired in the final product. Comparison is made with melts made with the volatile species not as part of an amorphous frit, i.e., as a raw batch component.

TABLE VIII

	Example 21	Example 22	Example 23
wt. % of Volatile Material in Frit	5.74% B_2O_3	0.62% F^-	1.38% P_2O_5
Initial wt.% of Volatile Material added into Batch Mixture in Frit	1.96% B_2O_3	0.21% F^-	0.47% P_2O_5
wt. % of Volatile Component Retained in Glass Product	1.67% B_2O_3	0.15% F^-	0.46% P_2O_5
% of Volatile Component Retained in Glass Product	85.2% B_2O_3	71.4% F^-	97.9% P_2O_5

TABLE IX

	Example 24	Example 25	Example 26
wt. % of Volatile Material in Frit	2.69% B_2O_3	0.20% F^-	0.39% P_2O_5
wt. % of Volatile Component Retained in Glass Product	1.66% B_2O_3	0.13% F^-	0.28% P_2O_5
% of Volatile Component Retained in Glass Product	61.7% B_2O_3	65.0% F^-	71.2% P_2O_5

CLAIMS

1. A process for making glass which comprises adding an amorphous glass frit containing normally volatile glass batch material into the glass forming components present in a glass melting furnace during molten glass formation, said volatile glass batch material being present in said amorphous glass frit in a percentage by weight at least two times as large as that desired in the final molten glass product.

2. A process according to claim 1, wherein said volatile batch material is present in said frit in a percentage by weight at least ten times as large as that desired in the final molten glass product.

3. A process according to claim 1 or 2, wherein said volatile batch material incorporated in said frit is selected from the group consisting of selenium, lead oxide, zinc oxide, boron oxide, sulphates, fluorides, chlorides, bromides, iodides, phosphates, and suitable mixtures thereof.

4. A process according to claim 3, wherein said selenium is present in said frit in an amount of at least about 1% by weight.

5. A molten glass product present in a glass melting furnace which is the product of components comprising an amorphous glass frit comprising a normally volatile batch material being present in said amorphous glass frit in a percentage by weight at least two times as large as that desired in the final molten glass product.

6. A molten glass product according to claim 5, wherein said volatile batch material is present in said frit in a percentage by weight at least ten times as large as that desired in the final molten glass product.

7. A molten glass product according to claim 5 or 6, wherein said volatile batch material incorporated in said frit is selected from the group consisting of selenium, lead oxide, zinc oxide, boron oxide, sulphates, fluorides, chlorides, bromides, iodides, phosphates, and suitable mixtures thereof.

8. A molten glass product according to claim 7, wherein said selenium is present in said frit in an amount of at least about 1% by weight.

INTERNATIONAL SEARCH REPORT

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PCT/GB 95/01953

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03C1/02 C03C1/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB,A,920 174 (UNITED GLASS LIMITED) 6 March 1963 see page 1, line 1 - line 42; claim 4 ---	1-8
X	US,A,3 628 932 (INOUE) 21 December 1971 cited in the application see column 1, line 43 - line 56 see column 2, line 17 - line 20 ---	1-8
X	US,A,4 521 523 (AUBOURG) 4 June 1985 see column 1, line 56 - column 2, line 14 --- -/--	1-3,5-7

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 7850 Derwent Publications Ltd., London, GB; Class E32, AN 78-90313A & JP,A,53 127 517 (DAINIPPON TORYO KK) , 7 November 1978 see abstract ---	1-3,5-7
P,X	EP,A,0 618 177 (PPG INDUSTRIES) 5 October 1994 see page 2, line 34 - line 52 see page 3, line 15 - line 22 -----	1-8

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 95/01953

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
GB-A-920174		NONE		
US-A-3628932	21-12-71	BE-A-	726674	16-06-69
		DE-A-	1900296	28-08-69
		FR-A-	2000127	29-08-69
		GB-A-	1202852	19-08-70
US-A-4521523	04-06-85	NONE		
EP-A-618177	05-10-94	US-A-	5385593	31-01-95
		CA-A-	2118737	30-09-94
		JP-A-	7010592	13-01-95